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Analysis of Fuel Cycle Materials for Nuclear Forensics: Pre- and Post-detonation

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ORNL January 9, 2020

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Outline

- Introduction
- Background
- Pre-detonation nuclear forensics
- Post-detonation nuclear forensics

Introduction

- B.S. Chemistry from UMass Amherst
  - Bio-inorganic synthesis
- 2010 Radiochemistry Fuel Cycle Summer School at UNLV
  - Radiochemistry course with an emphasis on the nuclear fuel cycle
- 2011 ACS Summer School in Nuclear and Radiochemistry
  - Brookhaven National Lab
  - Focus on nuclear medicine and nuclear fuel
- Ph.D. from UNLV in Radiochemistry
  - Dr. Ken Czerwinski
  - Synthetic actinide chemistry
  - Nuclear forensics
- At LANL since 2014
  - Dr. Jaqueline Kiplinger
    - Organoactinide synthesis
    - Air sensitive materials, glove-box work

Introduction

- Postdoctoral Work
  - Dr. Marianne Wilkerson
    - Analysis of fuel precursors
  - Dr. Sam Clegg
    - Gas FTIR analysis of stable isotopes of nitrogen
  - Dr. Keri Campbell and Dan Kelly
    - Uranium corrosion

- Funding
  - DHS NTNFC
  - LANL LDRD

- Large groups (>15 people)
- Small groups (<5 people)
- Mentor to high-school student

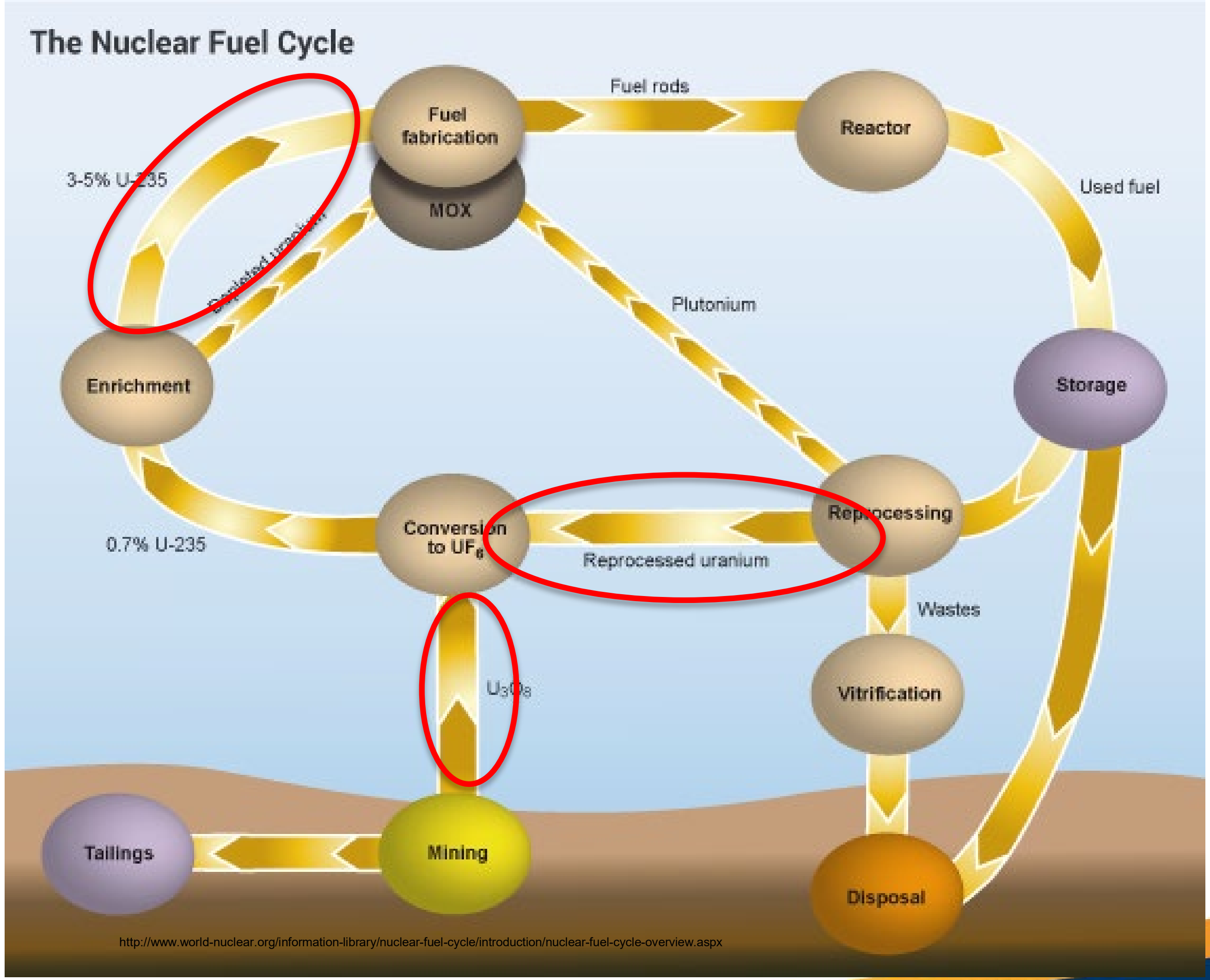
Background – Nuclear Forensics

- Nuclear forensics – the evaluation of signatures to determine the identification and provenance of nuclear material
  - Device, precursor materials, fuel, isotopic signatures

Part 1 – Pre-Detonation Forensics

Pre-Detonation Forensics

- Ammonium diuranate (ADU) and ammonium uranyl carbonate (AUC)
  are both present in multiple steps of the fuel cycle

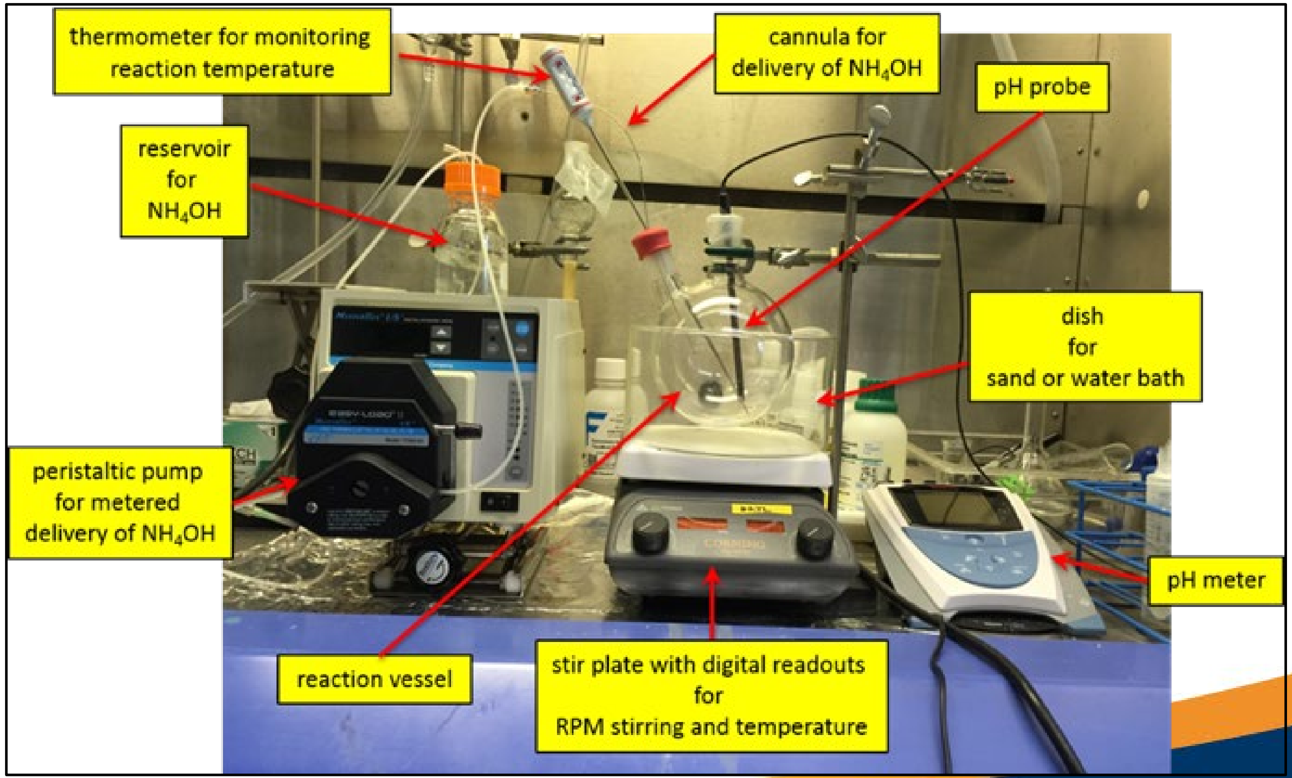


ADU – Ammonium Diuranate

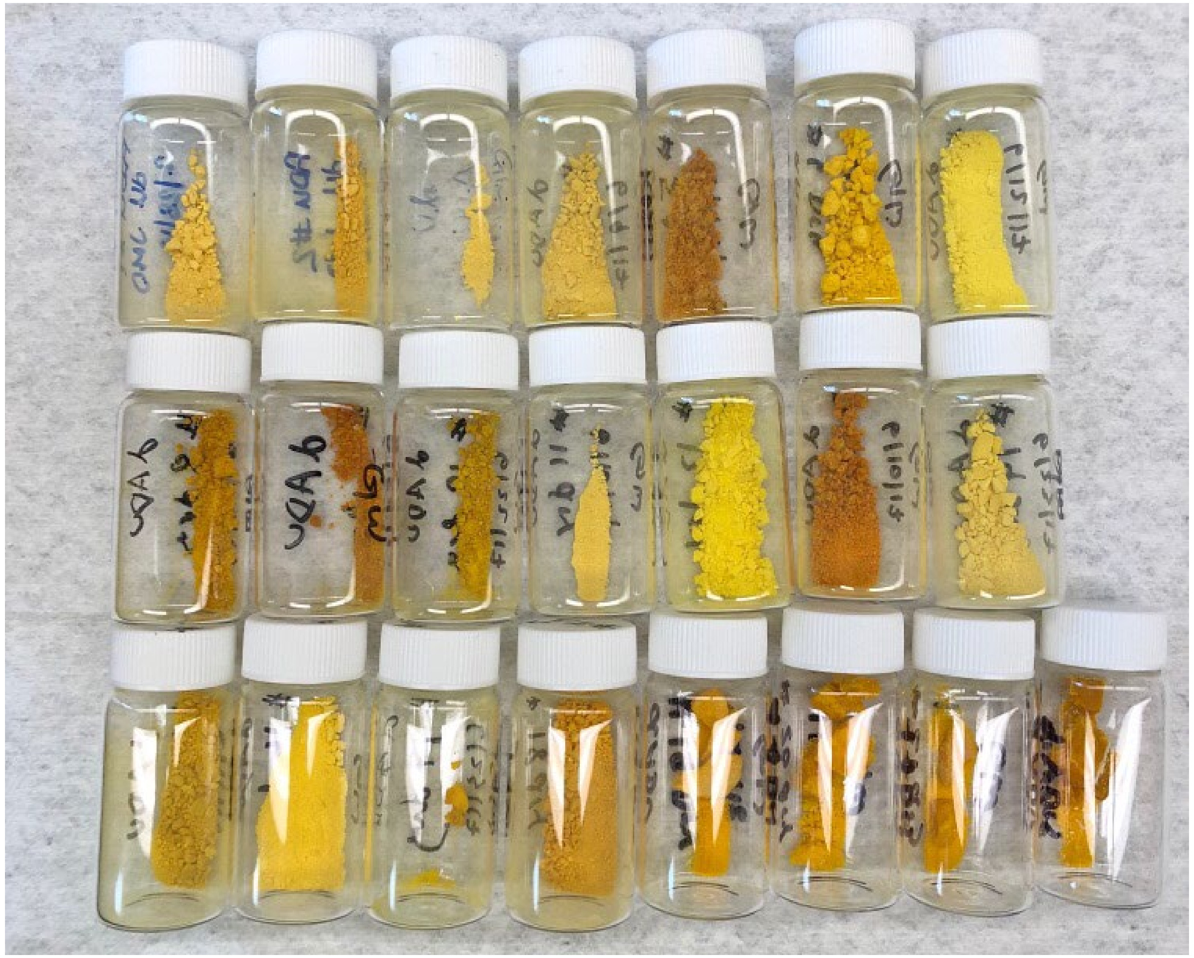
$$UO_2^{2+} + NH_4OH + HNO_3 \rightarrow UO_3 \cdot zNH_3 \cdot xH_2O + NH_4NO_3$$

STIR RATE (RPM)	[U] (MG/ML)	FINAL PH	FLOW RATE (ML/MIN)	TEMP (°C)
170	50	5	2.5	21.5
280	100	8	5	35
400	200	11	7.5	50

Statistical methods were used to go from 120 possible combinations to 22 experiments that would give the most diverse data set



ADU Characterization – Color



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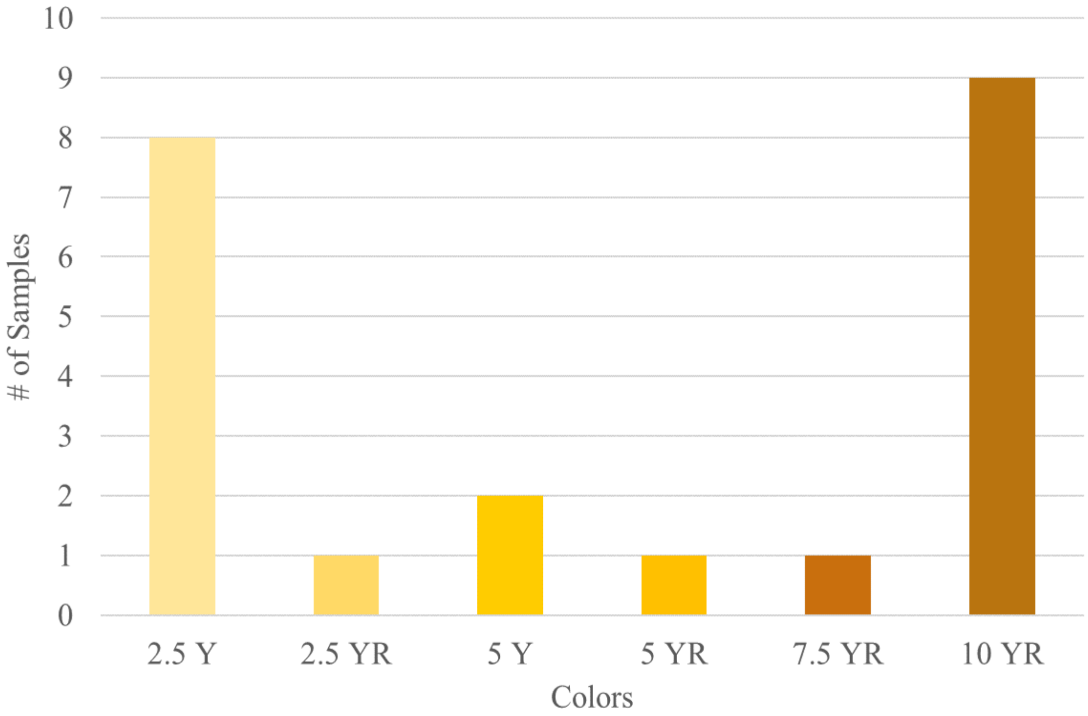
The Munsell Color Chart was used to define the colors of each compound based on hue (color), value (lightness), and chroma (purity).

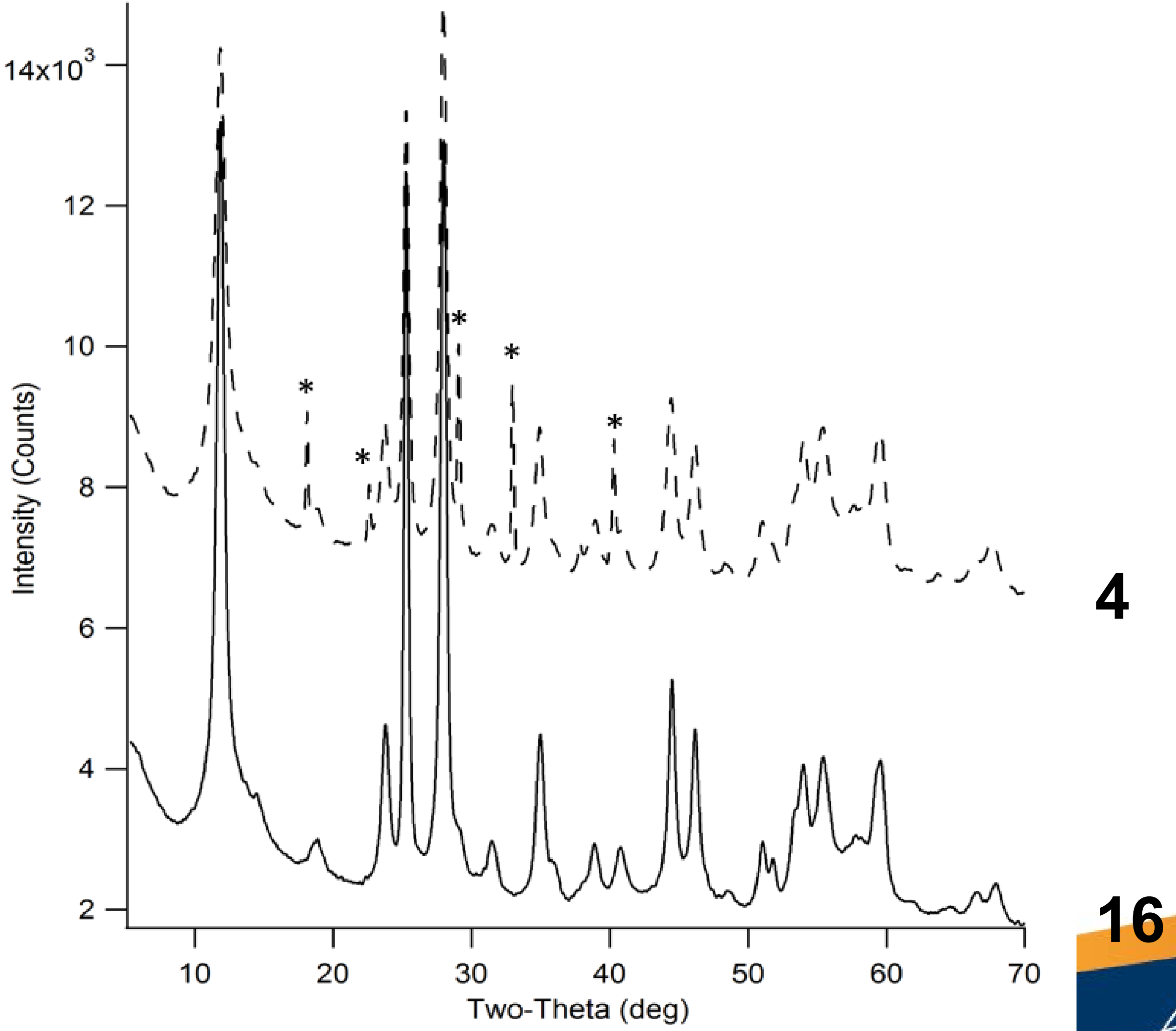


ADU Characterization - pXRD

- Powder XRD was used to identify the phases present in the materials
- One uranium containing phase: $UO_3 \cdot zNH_3 \cdot xH_2O$

(ICDD PDF No. 00-014-0340)

- Majority of compounds also show NH_4NO_3 (asterisks)
- Only two compounds, 3 and 16, did not contain NH_4NO_3 by XRD



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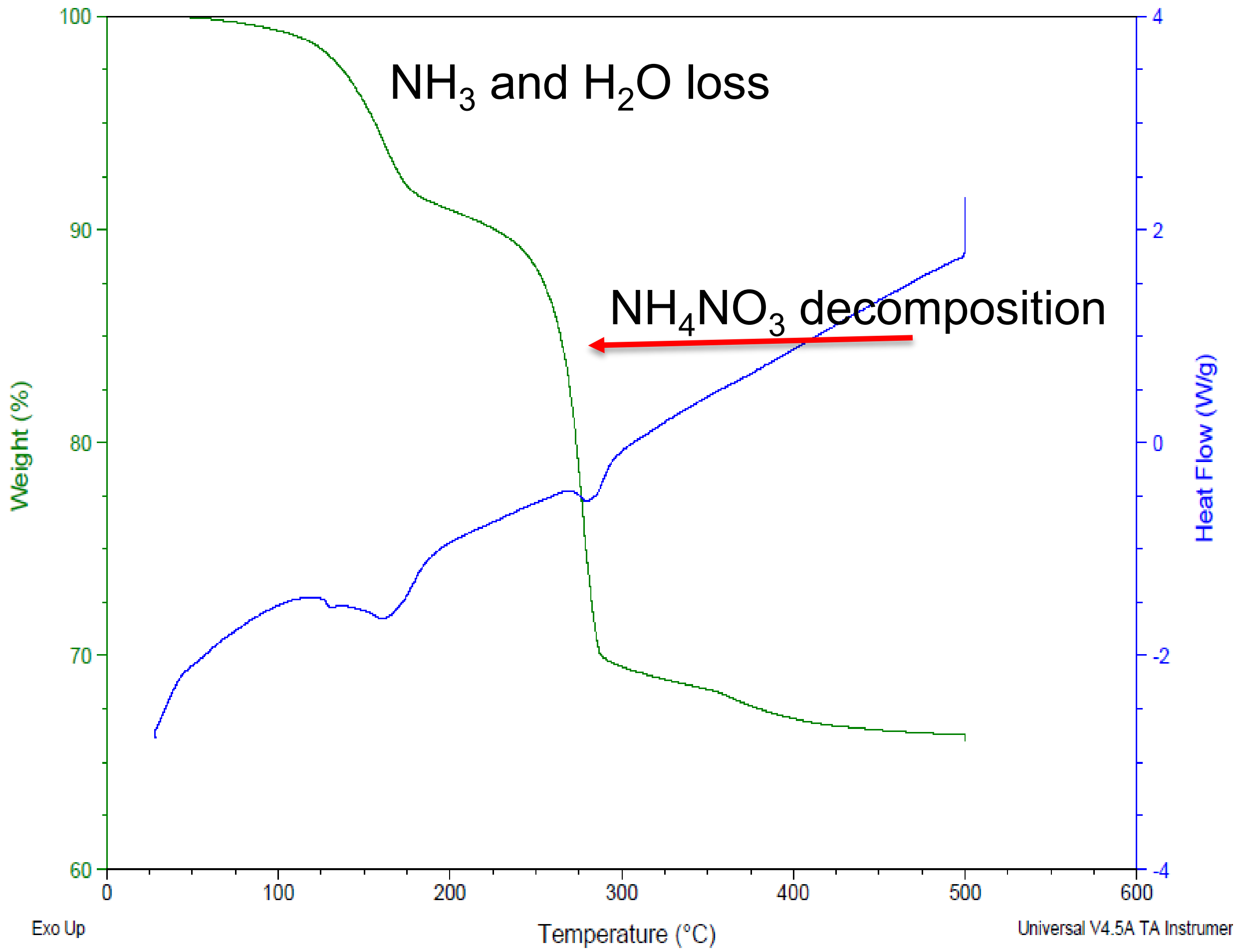
ADU Characterization – TGA/DSC



- TGA (green) shows weight loss as a function of temperature
- DSC (blue) shows endo- and exo-thermal events

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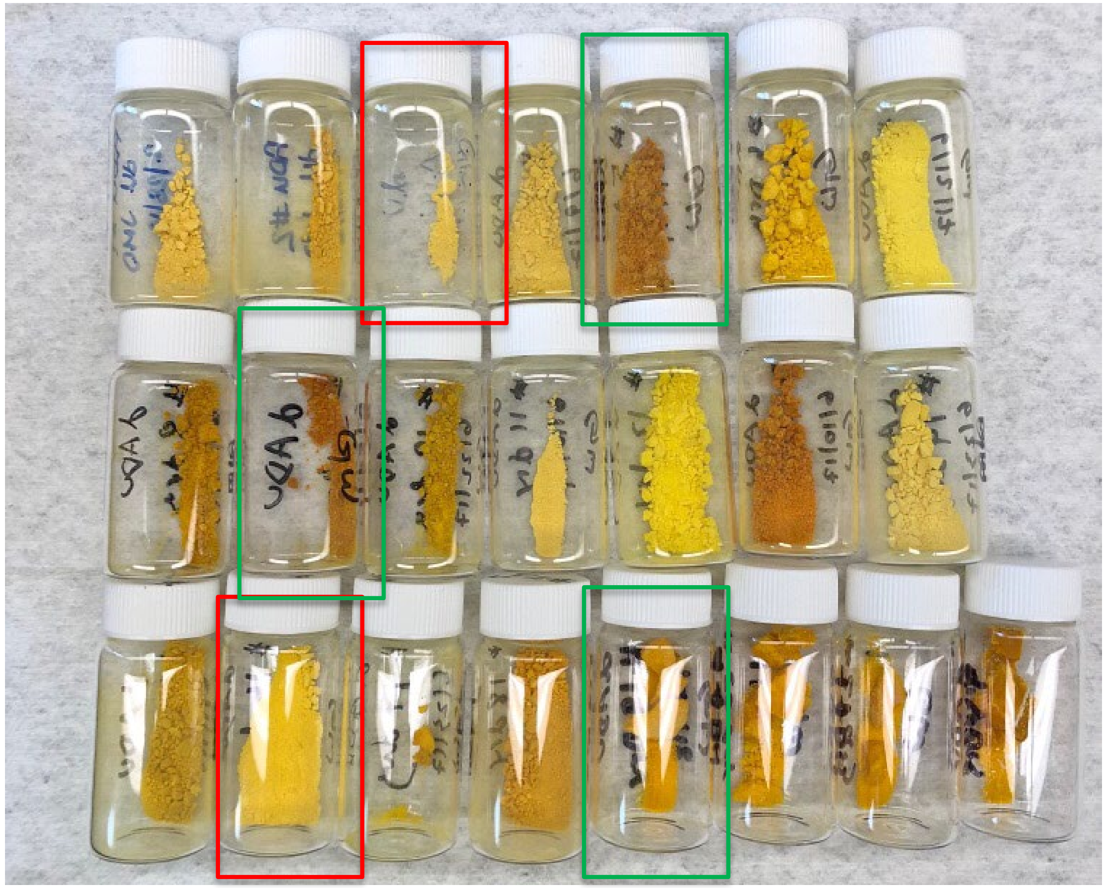
ADU Characterization – TGA/DSC

COMPOUND #	WEIGHT LOSS OF NH_4NO_3 (%)
1	9.82
2	19.00
3	4.90
4	19.41
5	35.39
6	28.22
7	11.94
8	26.01
9	28.77
10	21.53
11	17.41
12	21.24
13	26.12
14	12.09
15	18.72
16	4.88
17	20.70
18	20.40
19	30.86
20	23.11
21	17.68
22	25.02



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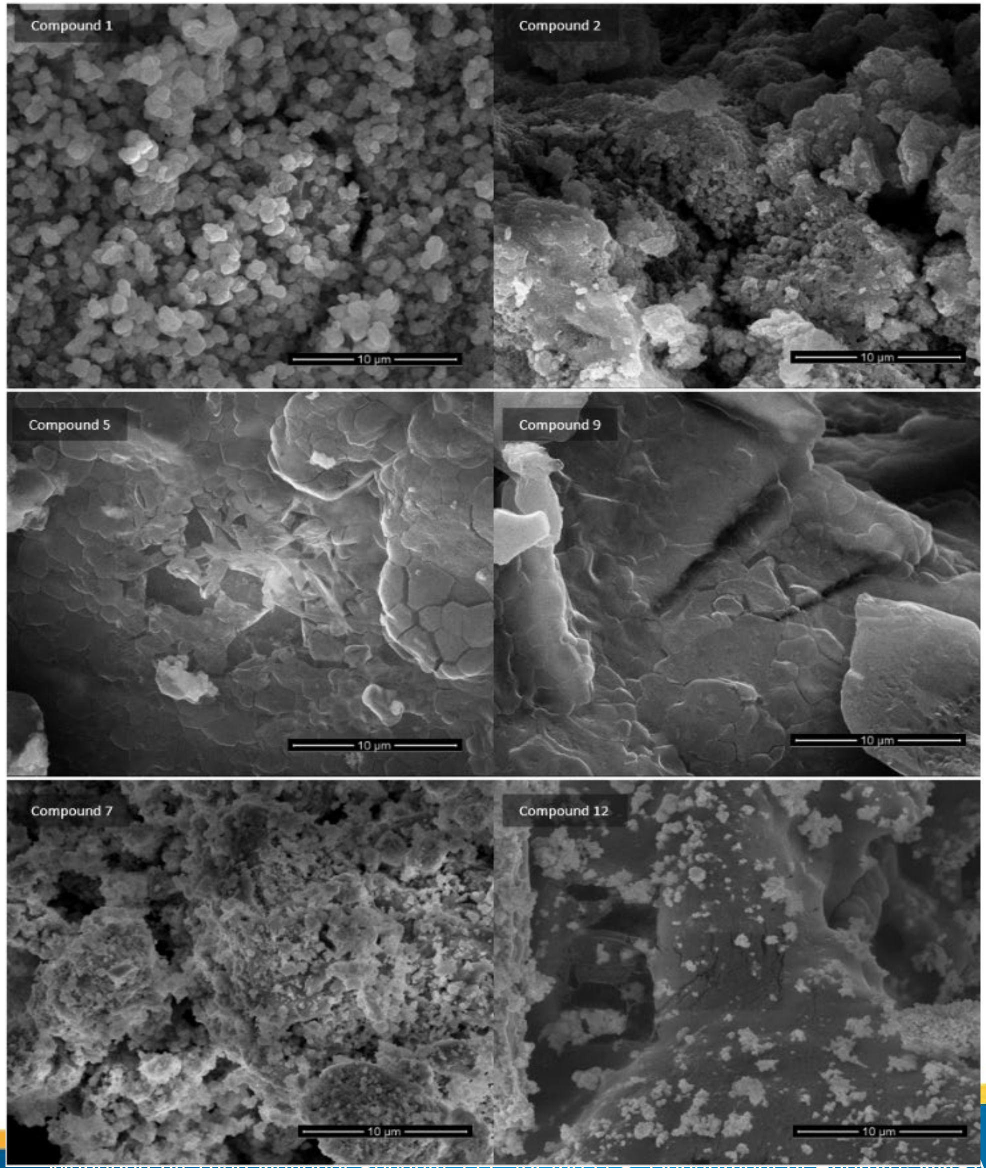
ADU Characterization – TGA/DSC

- Appears to be a correlation between the amount of NH_4NO_3 present and the color of the compound
- Light-colored compounds had high stir rates and often high concentrations of uranium
- Dark-colored compounds has high pH (i.e. more NH_4OH added) and low stir rates or uranium concentrations

ADU Characterization - SEM Analysis

Compound 1 had one of the lowest concentrations of NH_4NO_3 (9.82 %)



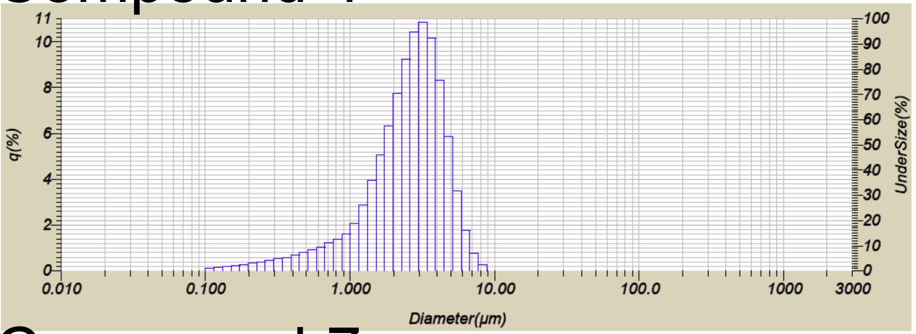
Compounds 5 and 9 had some of the highest concentrations of NH_4NO_3 (35.39 and 28.77 %)

Compounds 7 and 12 were middle of the road (11.94 and 21.24 %)

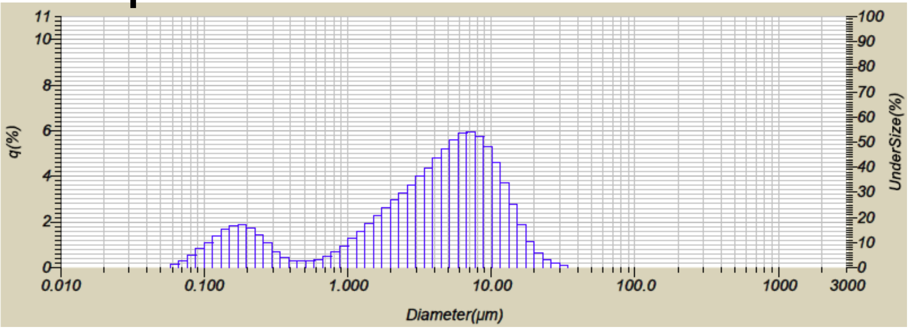
ADU Characterization – Particle Size

COMPOUND	MEDIAN DIAM. (UM) LIGHT-SCATTER	MEAN DIAM. (UM) LIGHT-SCATTER
1	4.834	4.741
2	3.746	3.818
3	2.2096	2.5062
4	2.6634	2.7756
5	2.1327	2.5772
6	8.1335	8.8301
7	4.3511	5.42
8	8.1135	8.513
9	11.867	12.657
10	3.7846	3.5019
11	1.5347	2.0429
12	3.7554	4.2099
13	2.8813	3.1654
14	2.5918	2.721
15	5.7682	5.8666
16	2.7171	2.6922
17	2.6574	2.6791
18	4.134	4.3449
19	4.923	5.338
20	2.698	2.677
21	3.153	3.163
22	2.975	3.017

Compound 4



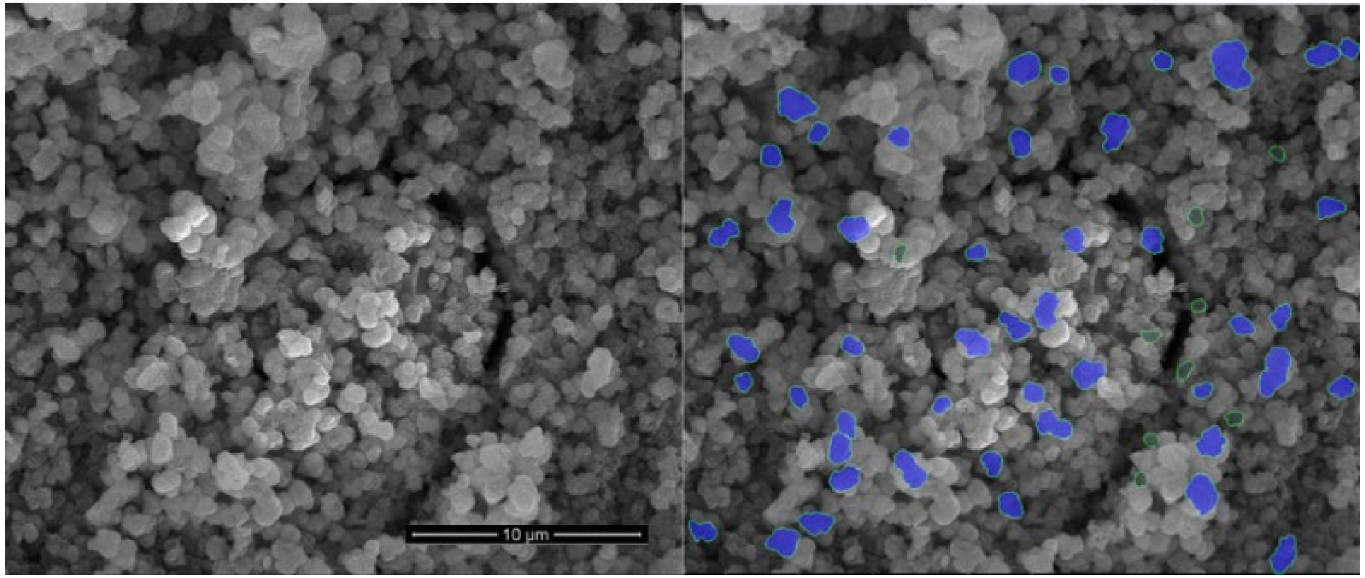
Compound 7



- In general, lighter colored compounds (4, 11, 16) have smaller particle sizes
- Darker compounds (9, 19) are larger
- Caveat – each sample was ground with a mortar and pestle prior to analysis

ADU Characterization - MAMA

- Morphological Analysis for Materials Attribution (MAMA) is a software designed at LANL for the purposes of analyzing morphological features of materials in SEM images
- MAMA measures 14 attributes, including pixel area, circularity, and ellipse aspect ratio



ADU Characterization - MAMA

- Compounds 1-18 were analyzed and the data was used to build a model to predict MAMA results for Compounds 19-22

COMPOUND #	19	20	21	22
AVG. MINOR ELLIPSE	2.41±1.62	2.50±2.39	2.65±2.54	2.41±1.67
PREDICTED MINOR ELLIPSE RANGE	0.120 – 1.08	0 – 0.811	0.530 – 1.35	0 – 0.671
AVG. DIAMETER ASPECT RATIO (DAR)	**1.61±0.64**	**1.55±1.34**	**1.54±1.04**	**1.63±0.54**
PREDICTED DAR RANGE	0.952 – 1.66	1.15 – 1.92	1.16 – 1.77	1.10 – 1.75
AVG. CIRCULARITY	**0.607±0.23**	**0.644±0.247**	**0.650±0.236**	**0.658±0.375**
PREDICTED CIRCULARITY RANGE	0.485 – 0.654	0.486 – 0.6856	0.5391 – 0.6936	0.514 – 0.6887
AVG. AREA CONVEXITY	**0.867±0.13**	**0.906±0.099**	**0.906±0.122**	**0.913±0.082**
PREDICTED AREA CONVEXITY	0.847 – 0.933	0.805 – 0.906	0.861 – 0.944	0.830 – 0.920

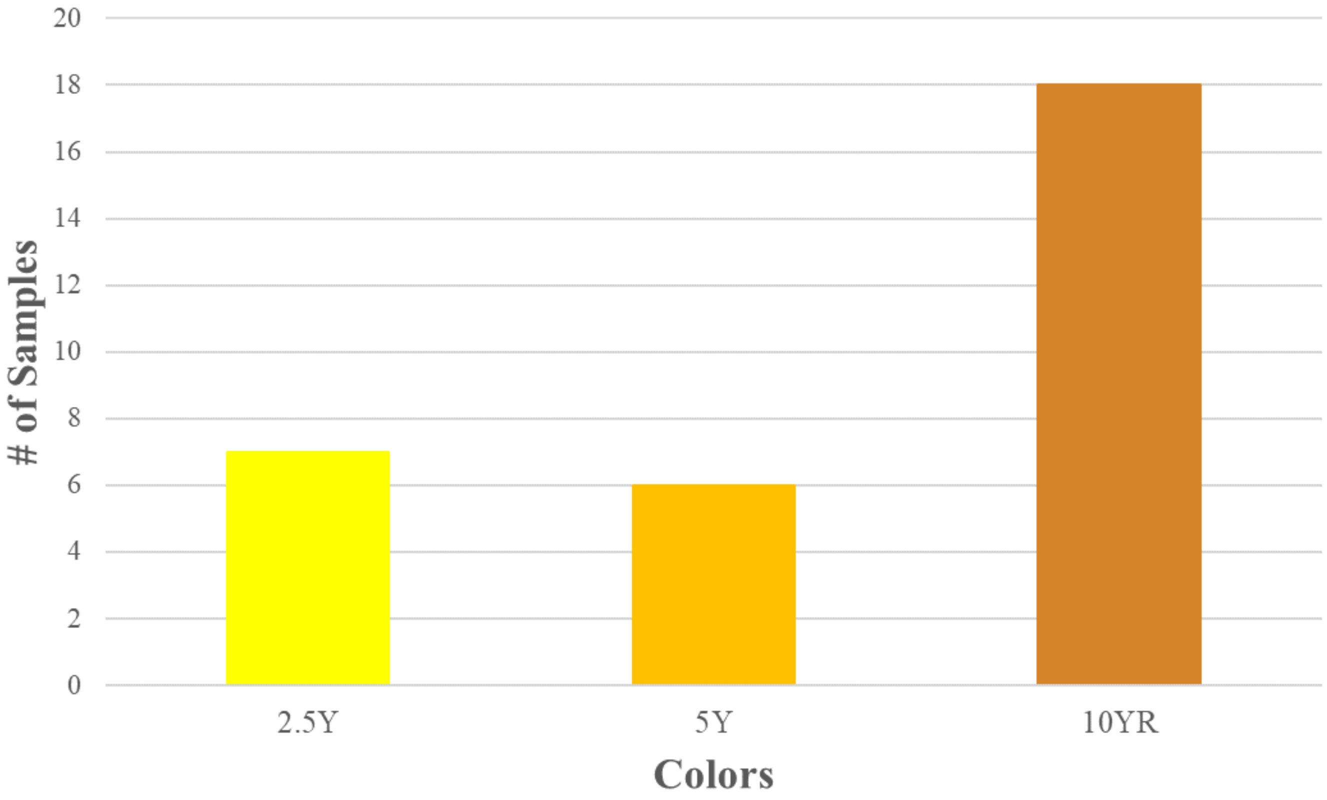
AUC – Ammonium Uranyl Carbonate

$$UO_2^{2+} + (NH_4)_2CO_3 + HNO_3 \rightarrow (NH_4)_4UO_2 \cdot zCO_3 \cdot xH_2O + yNH_4NO_3$$

[U] (mg/mL)	CO_3/U Ratio	Stir Rate (rpm)	Addn. Rate (mL/min)	Temp (°C)
50	3.5	170	2.5	21
75	4.25	280	5	35
100	5.0	400	7.5	50

- Synthetic method similar to ADU
- Statistical model used to choose 31 materials to get the most diverse data set
- Complete data set contains 29 independent materials and 2 sets of repeated conditions

AUC Characterization - Color



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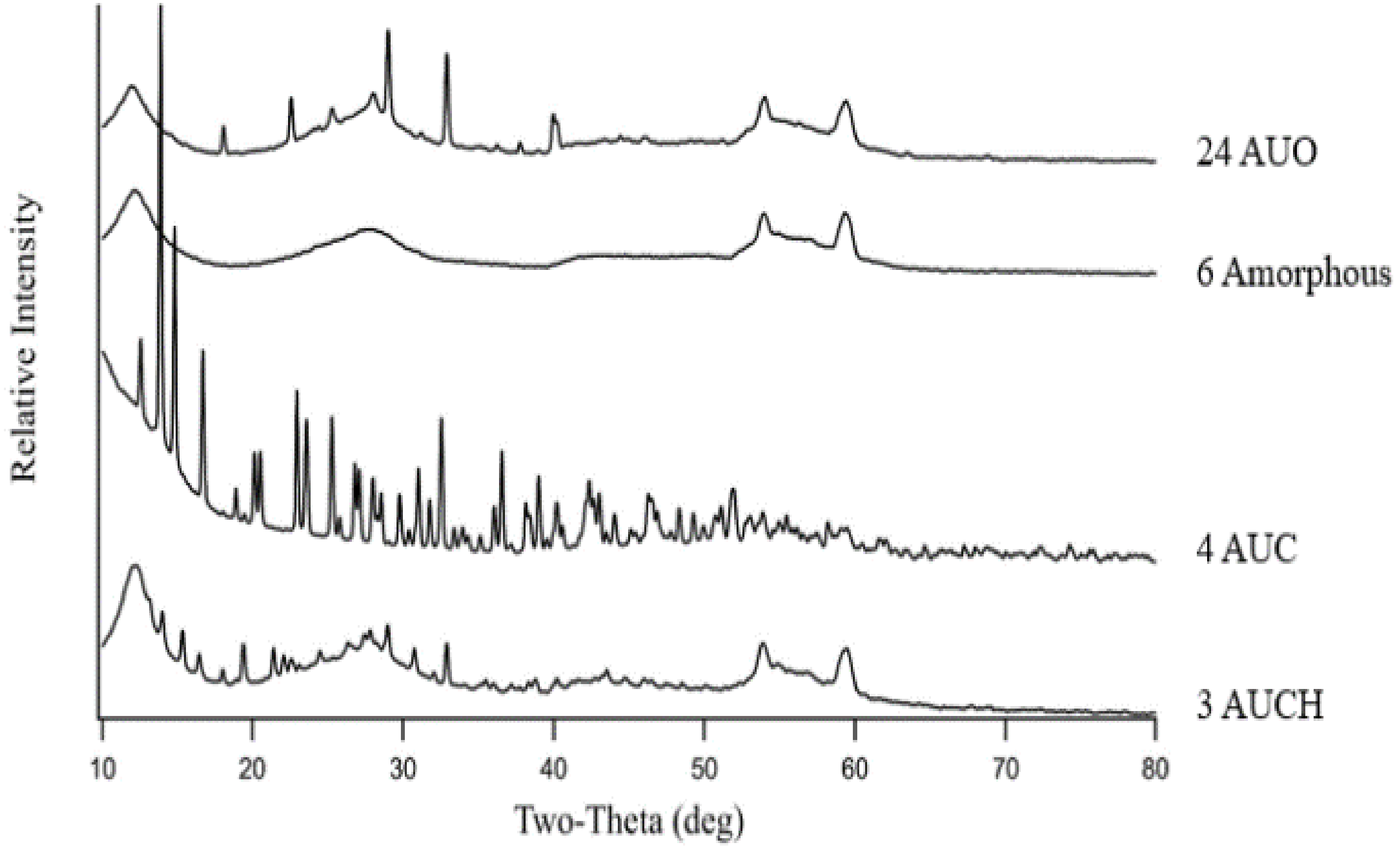
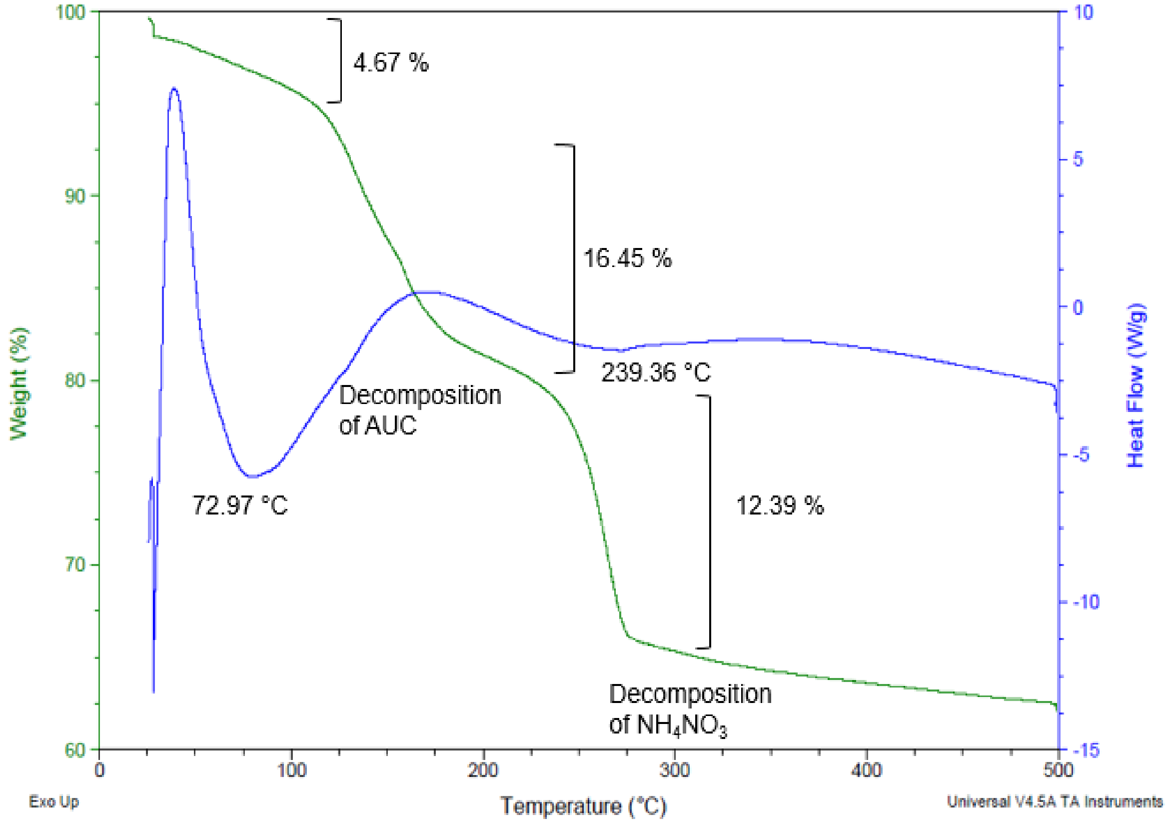
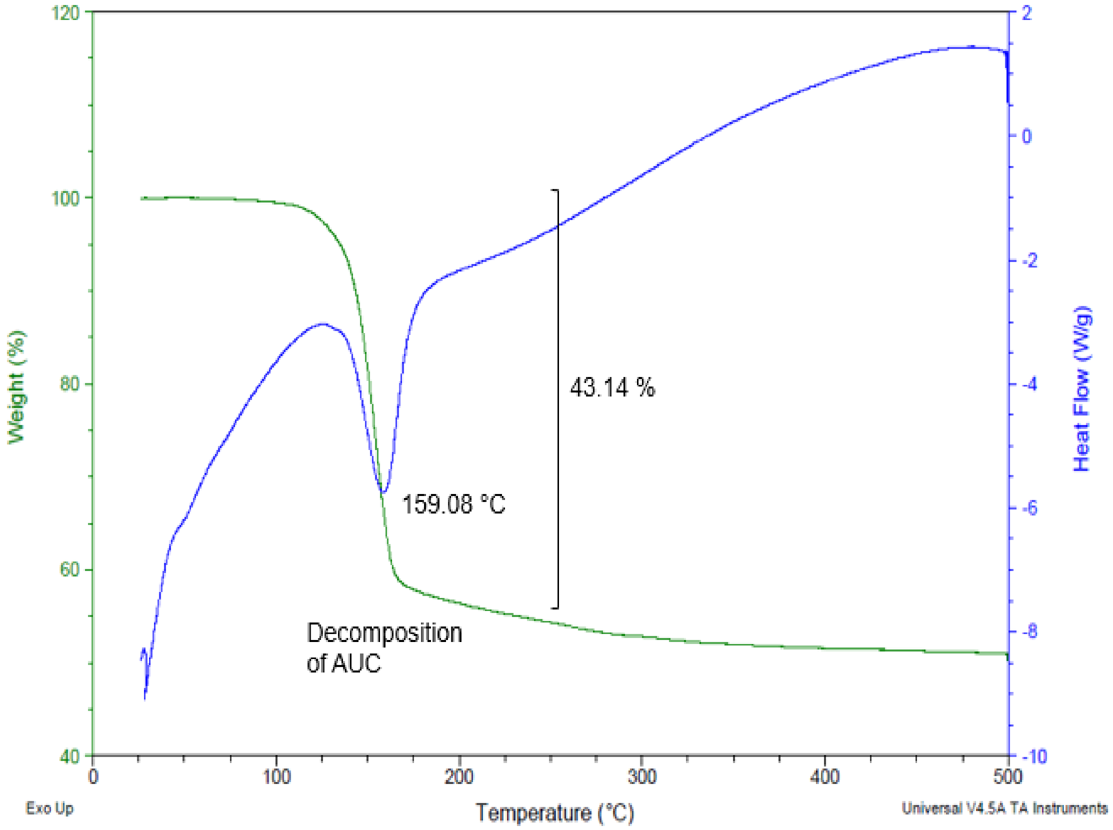
AUC Characterization - pXRD

- XRD patterns show four distinct uranium phases in the data set
- 25 compounds contain NH_4NO_3



AUC Characterization – TGA/DSC





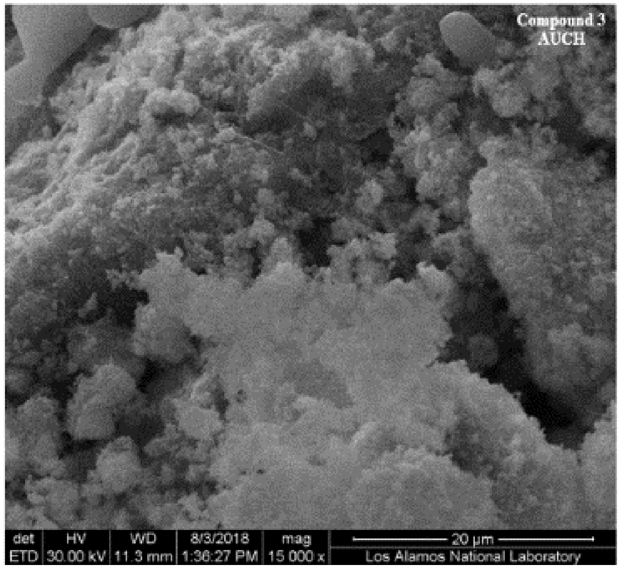
Compound 3 - AUCH

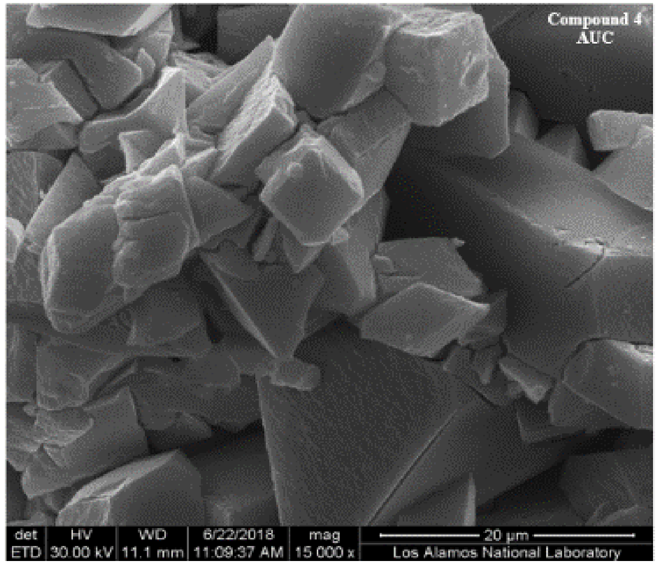
Compound 4 – AUC; no NH_4NO_3

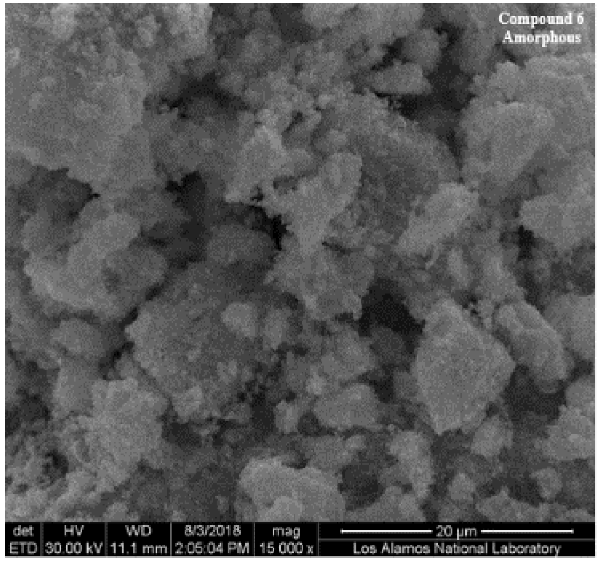
AUC Characterization – TGA/DSC

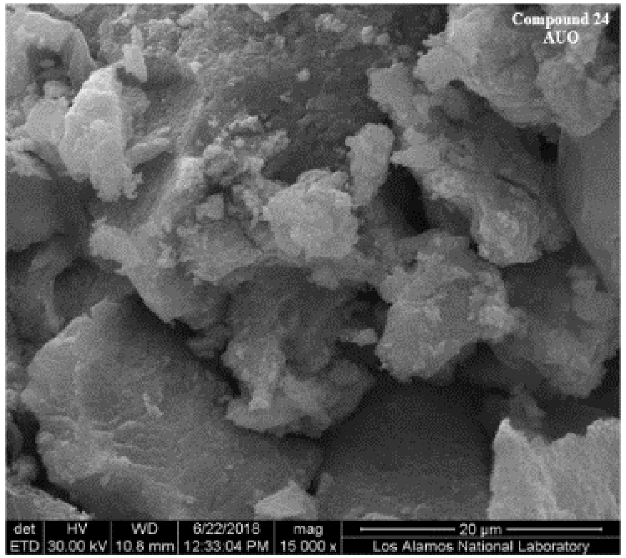
Compound	%NH_4NO_3	Color (Hue Value/Chroma)	CO_3/U ratio	Type
1	7.02	5Y 8/8	3.5	Am
2	6.7	5Y 8/8	5	Am
3	12.39	5Y 8/8	3.5	AUCH
4	0	5Y 8/6	5	AUC
5	17.84	10YR 8/8	4.25	AUCH
6	8.53	2.5Y 8/8	3.5	Am
7	26.55	10YR 8/8	3.5	Am
8	28.56	10YR 8/8	5	AUCH
9	11.02	5Y 8/8	4.25	AUC
10	10.19	10YR 8/8	3.5	AUCH
11	27.82	10YR 8/8	5	Am
12	7.46	5Y 8/8	4.25	AUC/ AUCH
13	22.46	10YR 8/8	3.5	AUCH
14	13.76	2.5Y 8/8	5	AUCH
15	11.85	2.5Y 8/8	3.5	Am
16	21.42	10YR 8/8	4.25	Am
17	20.33	10YR 8/8	4.25	Am
18	22.51	10YR 8/8	5	Am
19	24.23	10YR 8/8	5	Am
20	16.95	10YR 8/8	4.25	Am

AUC Characterization - SEM









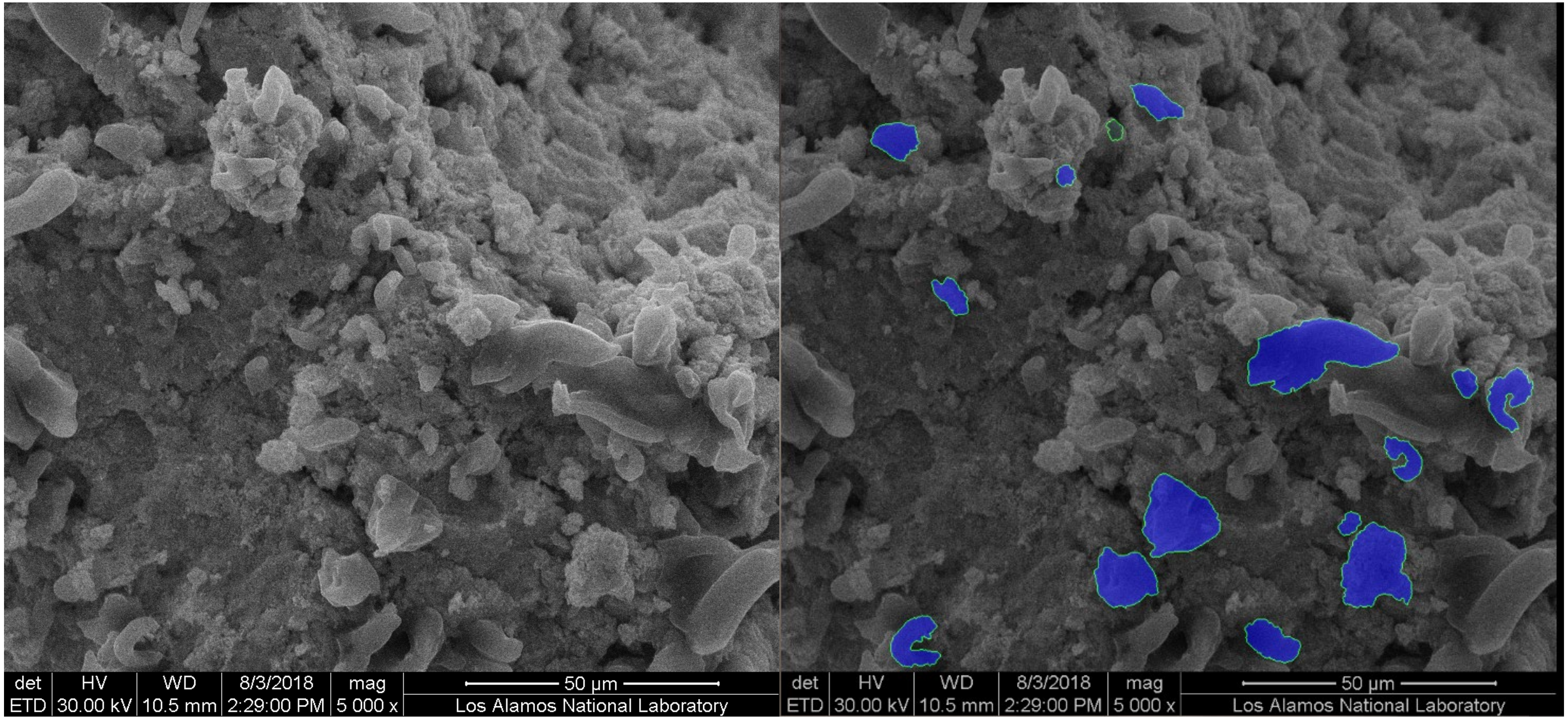
Compound 3 – AUCH
12.39% NH_4NO_3

Compound 4 – AUC
0% NH_4NO_3

Compound 6 – Amorphous
8.53% NH_4NO_3

Compound 24 – AUO
TBD

AUC Characterization - MAMA



Compound 13 – AUCH with 22.46% NH_4NO_3

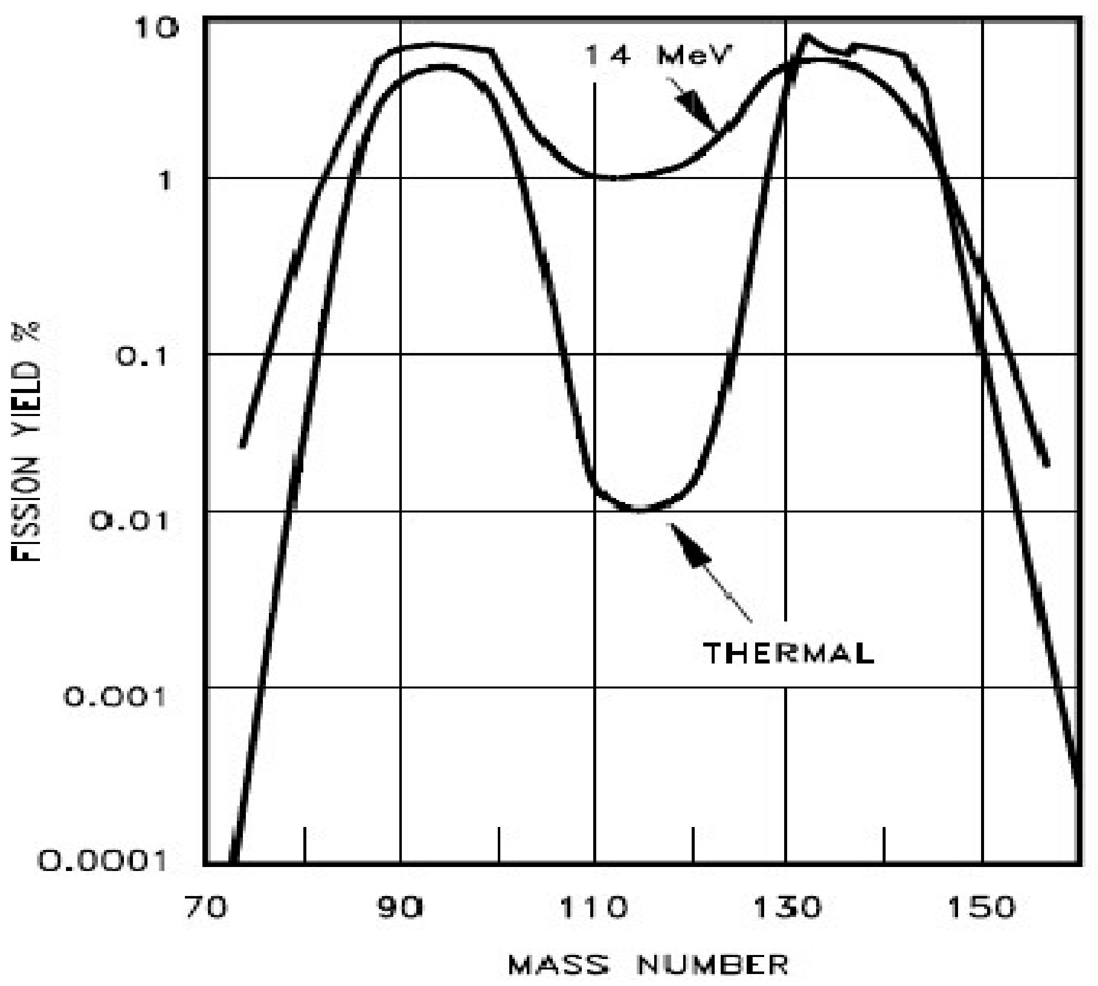
ADU and AUC Conclusions

- ADU and AUC are precursors to UO_2 fuel and could be interdicted
- Correlations between synthetic conditions and physical, chemical, and morphological characteristics could help identify provenance of stolen material
- It appears that there is no straightforward correlation, however several reaction conditions together seem to lead to changes
  - Morphology, NH_4NO_3 concentration, color
- Statistical models can help us predict measured attributes from MAMA based on combinations of reaction conditions
  - Model has limitations and potential bias

Part 2 – Post-detonation Forensics

Post-detonation Forensics

- Major component of post-detonation analysis is looking at fission yields
- Yields, particularly for higher mass numbers, can help identify the type of device



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Prelas, M. A.; Weaver, C. L.; Watermann, M. L.; Lukosi, E. D.; Schott, R. J.; Wisniewski, D. A. *Progress in Nuclear Energy* **2014**, *75*, 117.

Goal

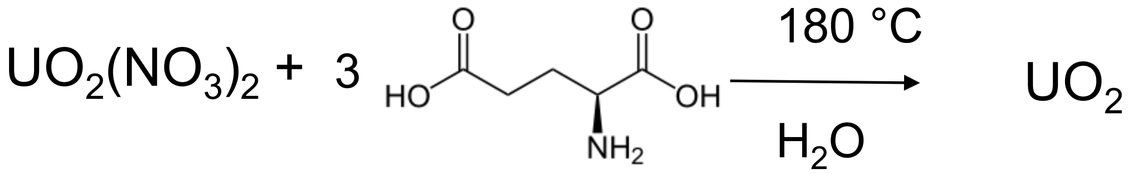
- Goal: To create actinide target materials for the rapid separation of fission products without the need to dissolve the entire target
  - Proof-of-principle to advance the library of fission product ratios for various actinides
- Procedure: To prepare and irradiate a target material, then rapidly separate and measure the fission products

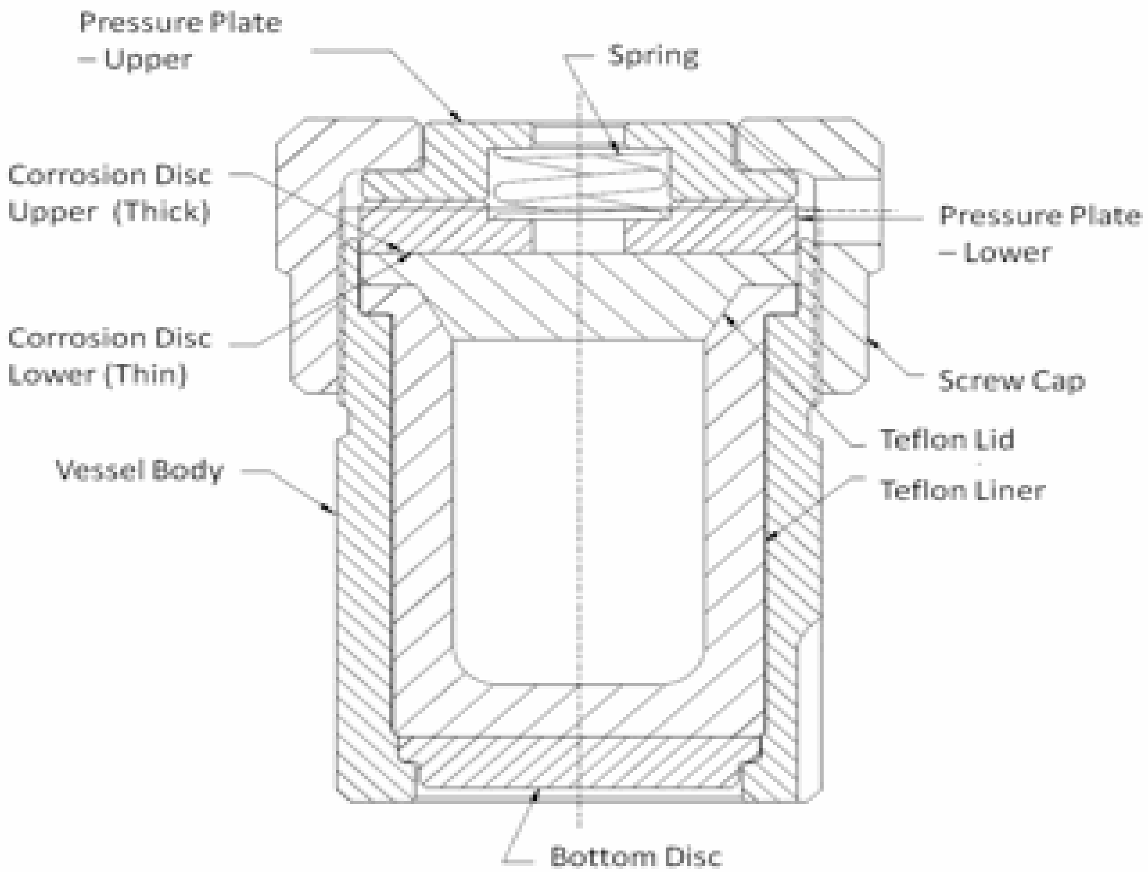
UO_2 Fuel

- UO_2 has been used in fuel, target materials, and fission product analysis for decades
  - Literature references site these particle sizes between 20 µm and 200 mm
- Dissolution of materials is generally done in HNO_3 and/or HCl at acid concentrations > 1M

UO_2 Production – A Novel Method

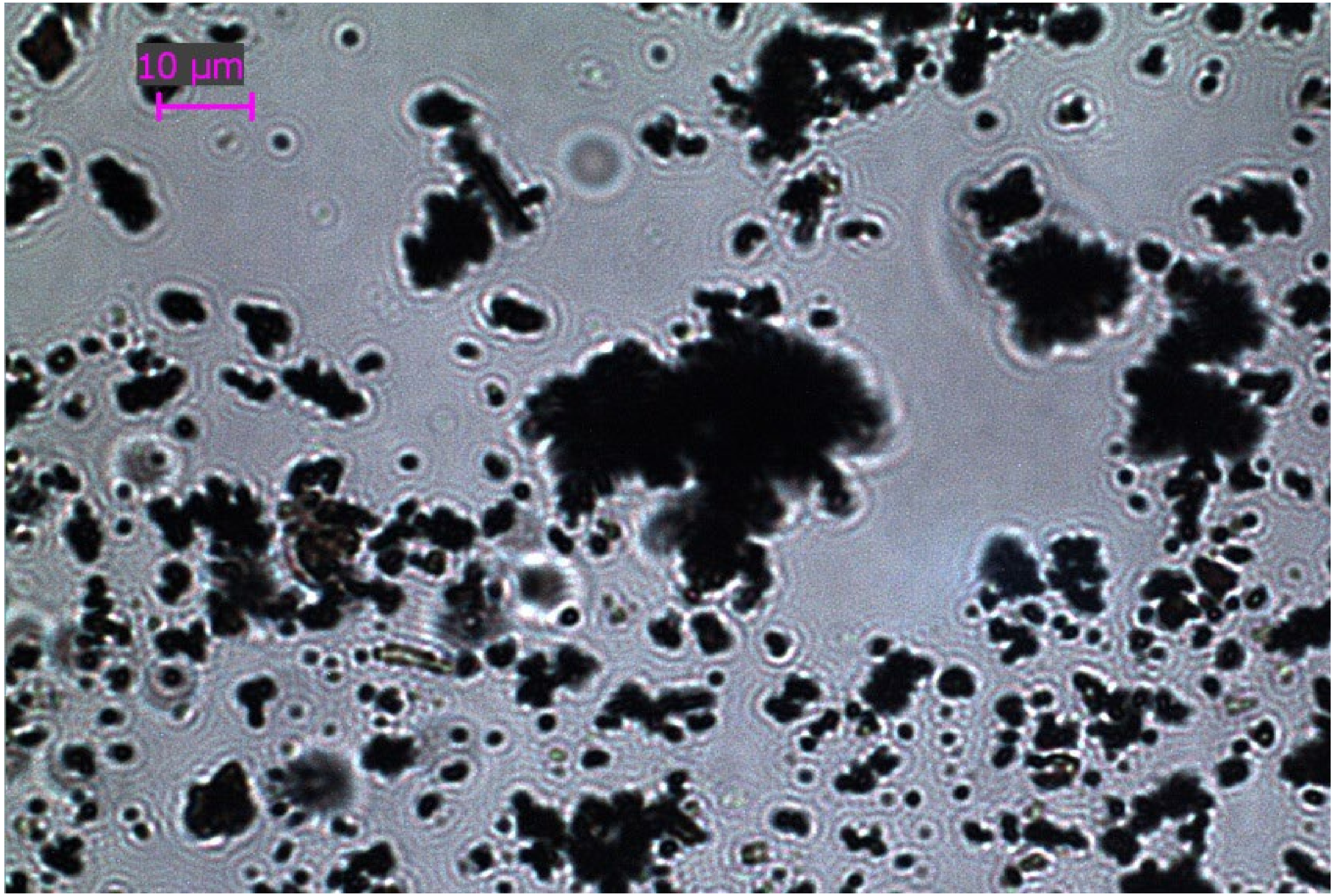
- Hydrothermal synthesis





Blakemore, P.; Oregon State University: Corvallis, Oregon, 2017; Vol. 2017, p image of parr bomb.

UO_2



Dorhout *et.al JRNC,* **2019**, *319*, 1291.

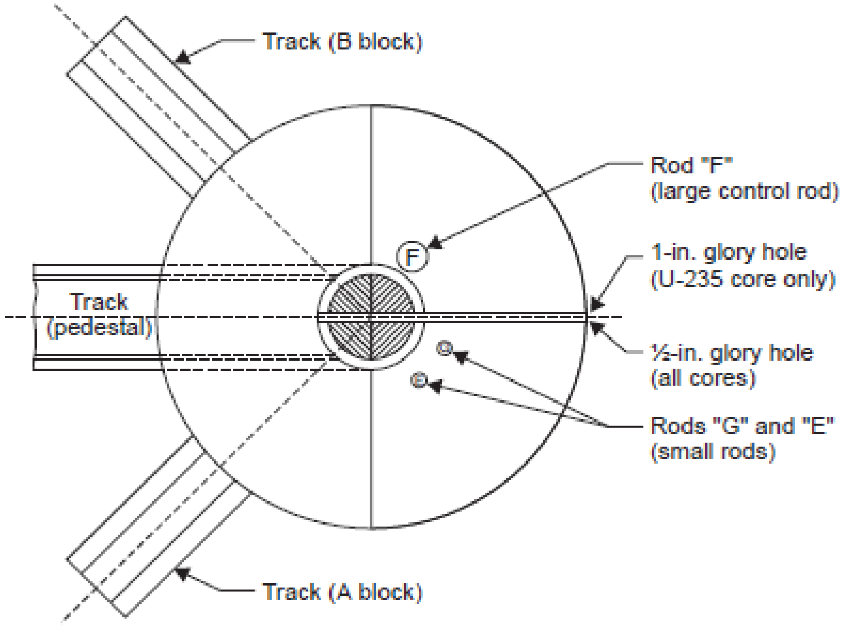
UO_2 Target Production

- KBr chosen as a secondary matrix to trap fission products (3:1 KBr:UO_2 by mass)
- Targets were 25 mg dUO_2
- Pressed into a 6 mm pellet
- Sealed in Al sample holder

Dorhout *et.al JRNC,* **2019**, *319*, 1291.

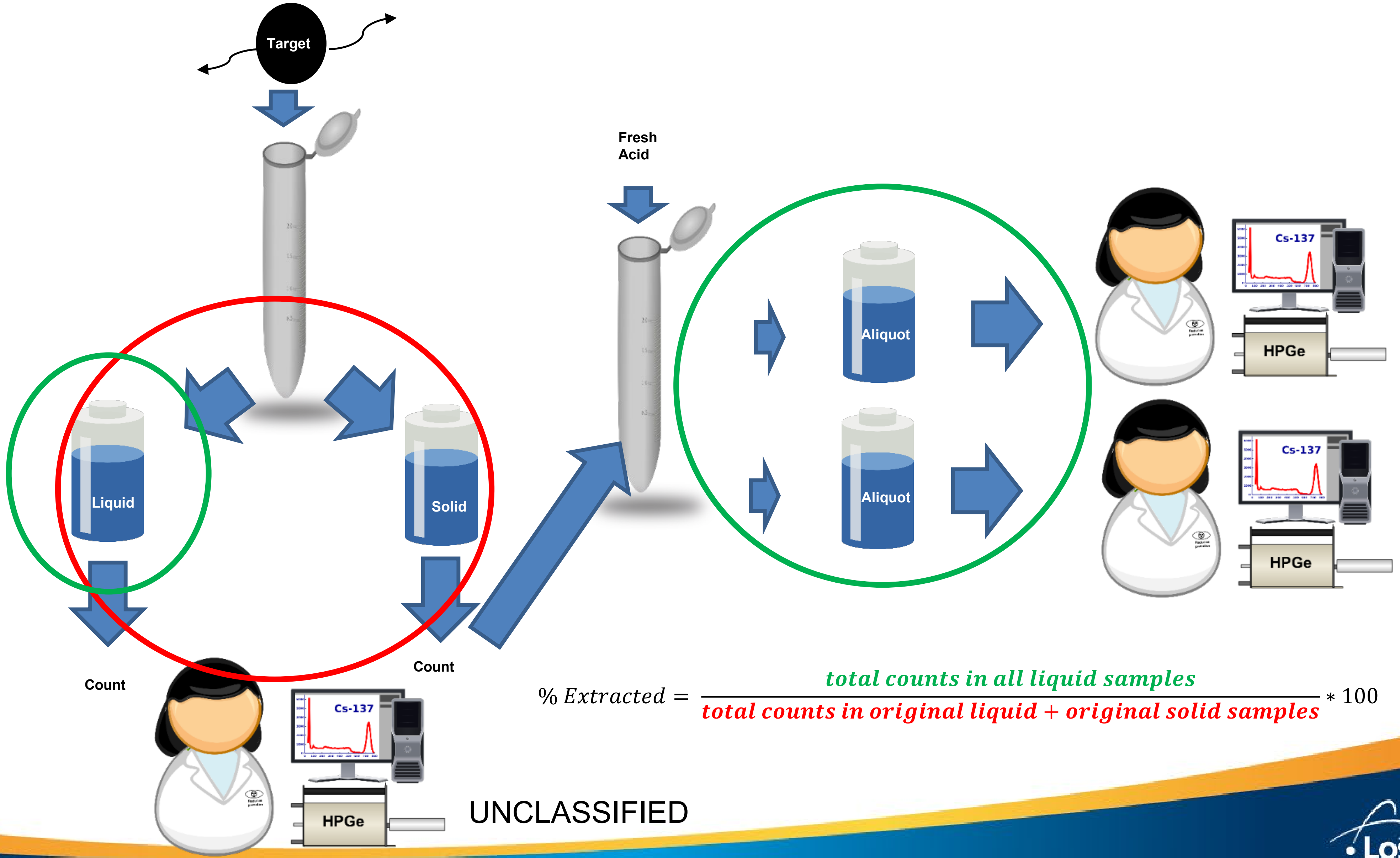
UO_2 Irradiation

- Flattop is a critical assembly device made of HEU at the Nevada National Security Site



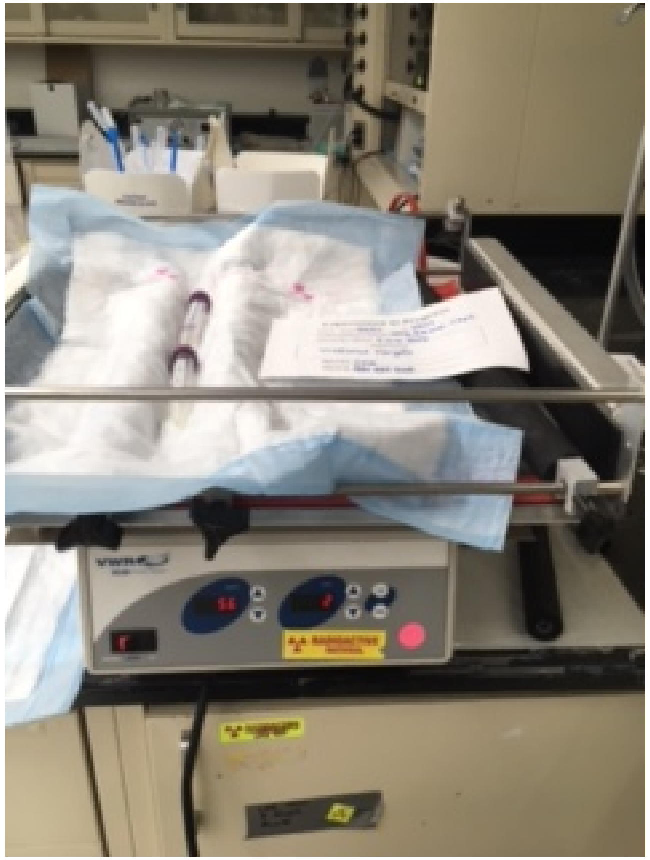
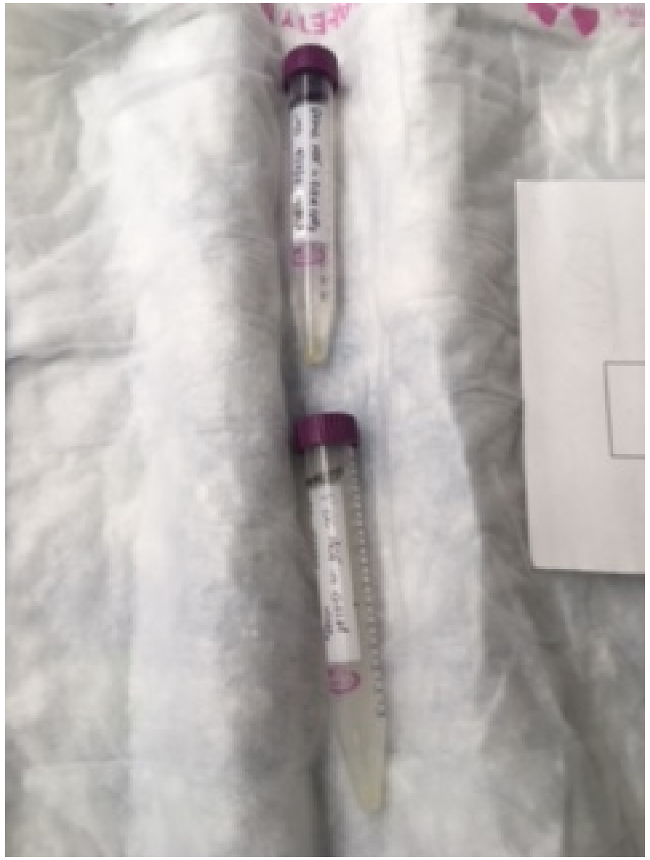
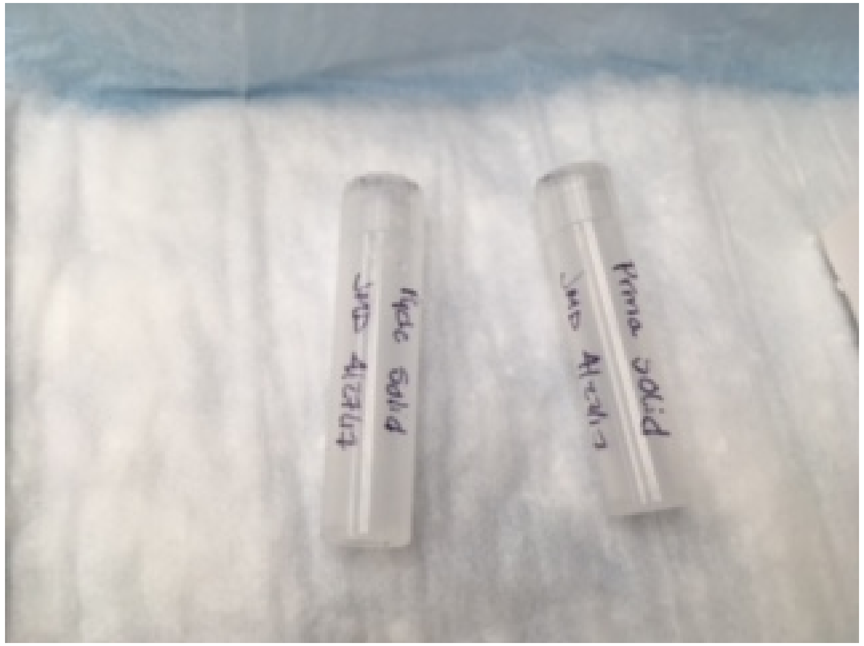
Brewer, R. W.; McLaughlin, T. P.; Dean, V. *Uranium-235 Sphere Reflected by Normal Uranium Using Flattop*, Nuclear Energy Agency, 1999.

Rapid Separation



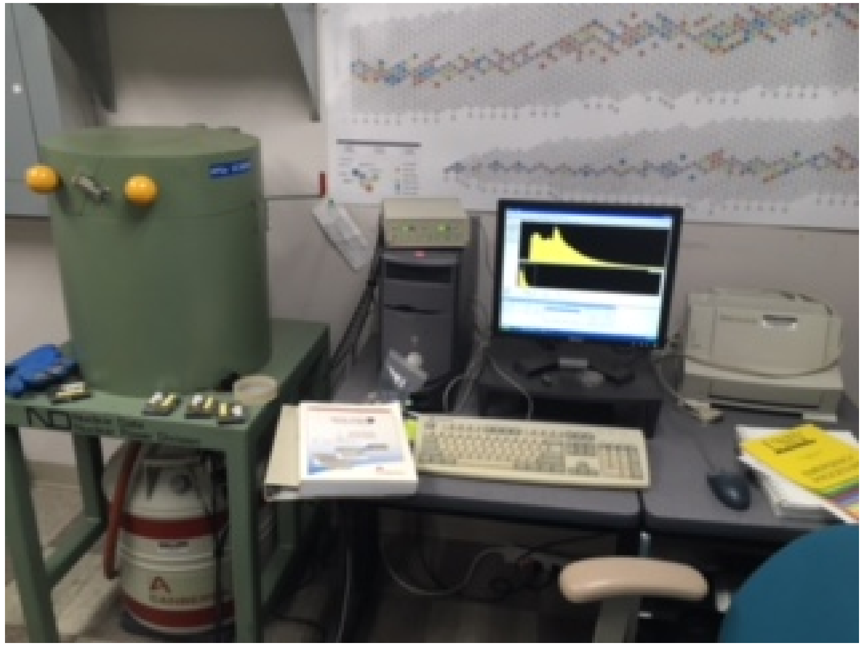
$$\%\ Extracted = \frac{\textit{total counts in all liquid samples}}{\textit{total counts in original liquid + original solid samples}} * 100$$

Rapid Separation

Gamma Counting

- HPGe and BEGe detectors used in experiments
- Each sample (plus a background) was counted for the same amount of time
- Down-side: only gamma emitting isotopes are identifiable



Results – Flattop

- Irradiations done on multiple samples
- Five UO_2 samples studied
  - Four samples of $3KBr:UO_2$
    - Each contacted with a different acid
      - 0.01 M HCl, 0.1 M HCl, 0.01 M HNO_3, or 0.1 M HNO_3
  - One sample with no KBr present
    - How important is secondary matrix?
    - Contacted with 0.01 M HNO_3

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Results

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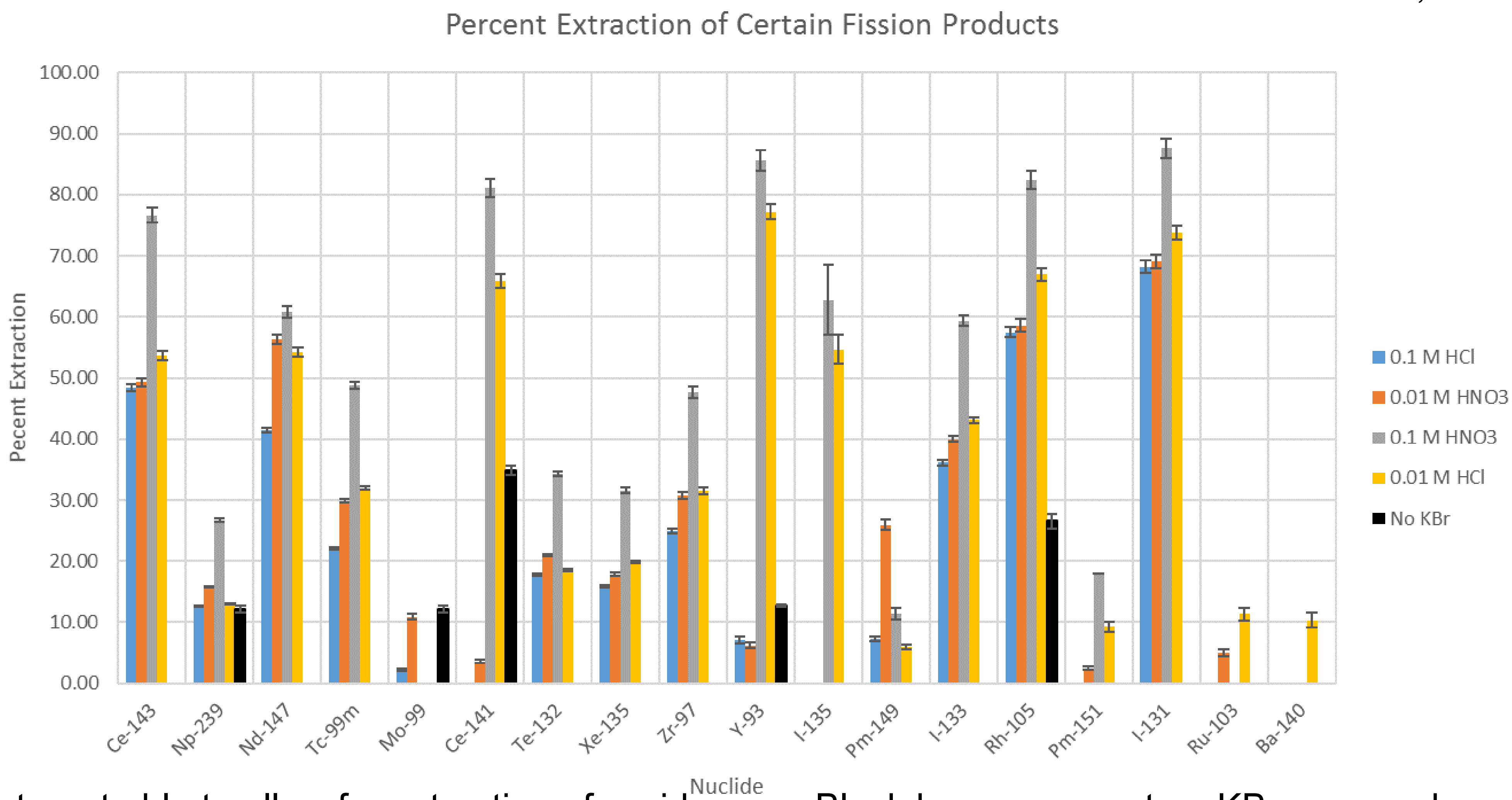

- Each target able to allow for extraction of a wide variety of fission products
- 0.1 M HNO_3 data is artificially high
- Black bars represent no KBr – secondary matrix does have an affect

Issues

- KBr is easy to work with and remove with dilute acid, but it is activated in the neutron flux to give ^{82}Br
  - Many gamma energies
  - Short half-life, high activity
  - Could be resolved by using a different secondary matrix
- Targets were irradiated at different times under different conditions
  - Cannot compare activities extracted
  - Must compare percent extraction

Conclusions

- Proof-of-concept shown
- 0.01 M HNO_3 chosen as extractant for all future experiments
- Secondary matrix does seem to have a positive affect on extraction
- Different secondary matrix could make analysis easier

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  - Radiation and Safety Staff

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